

# Application of Chemometrics to PFGSE NMR in Polymer Systems: Impact of Multi-exponential Relaxation on DECRA Analysis

Todd M. Alam<sup>1</sup> and M. Kathleen Alam<sup>2</sup>

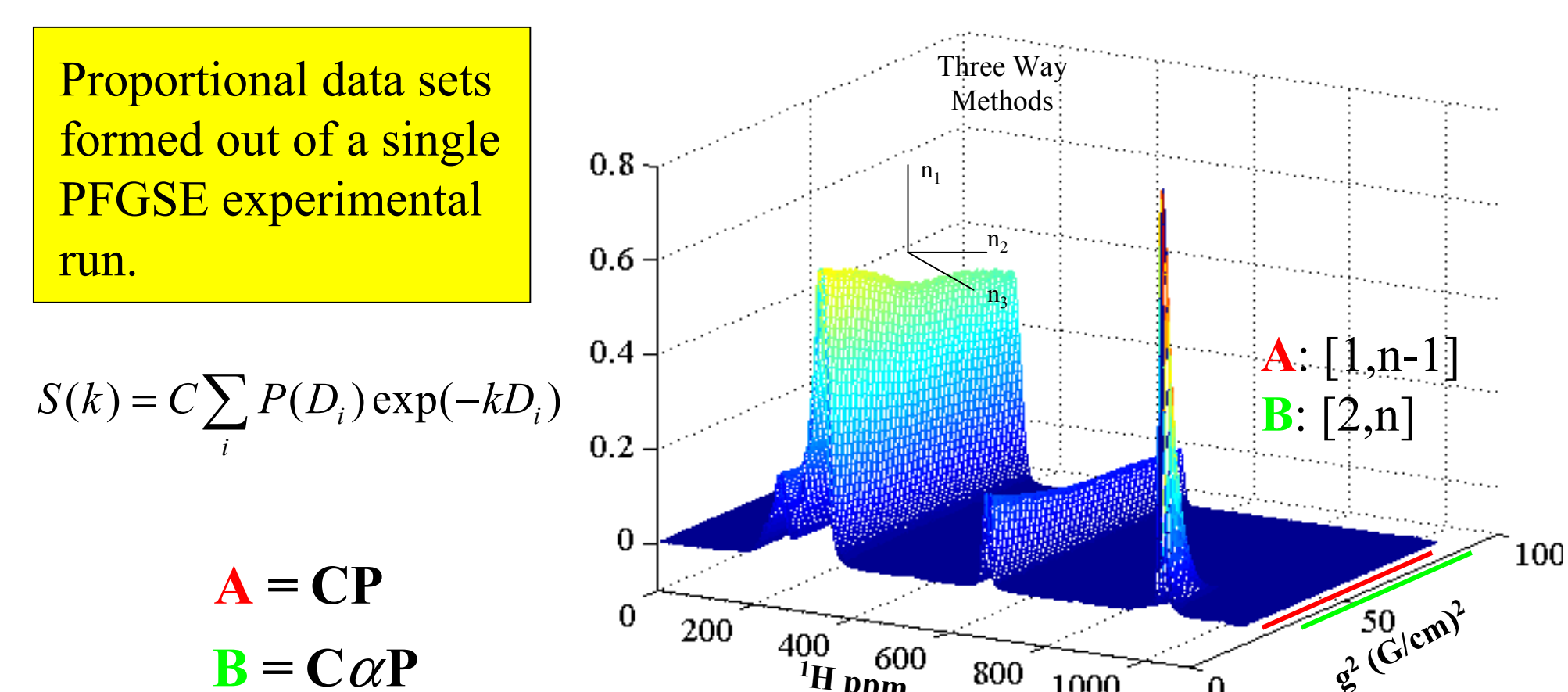
<sup>1</sup> Department of Organic Materials, <sup>2</sup>Department of Information, Discovery, Extraction and Analysis  
Sandia National Laboratories, Albuquerque, New Mexico 87185-0888

## Abstract

The use of chemometrics and multivariate techniques has proven to be a powerful tool for the analysis of pulse field gradient spin echo (PFGSE) NMR spectral data. This is especially true in complex systems such as polymer systems. This laboratory has utilized a range of chemometric techniques, including direct exponential curve resolution (DECRA), component-resolved NMR (CORE), and non-linear multiple curve resolution (MCR) techniques for the analysis of PFGSE NMR data of aged polymer systems. DECRA provides very fast analysis speeds even for very large relaxation data sets: and is therefore almost always our first choice of analysis techniques. The advantages and limitations of the DECRA algorithm are addressed. In particular, the spectral distortions and errors introduced by the polydispersity of the self-diffusion decay coefficient were investigated. Many of our initial naïve assumptions about the effects of polydispersity on the chemometric analysis of PFGSE NMR data sets are shown to be misguided.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.*

## PFGSE Analysis of Polymers



## Polydispersity Effects

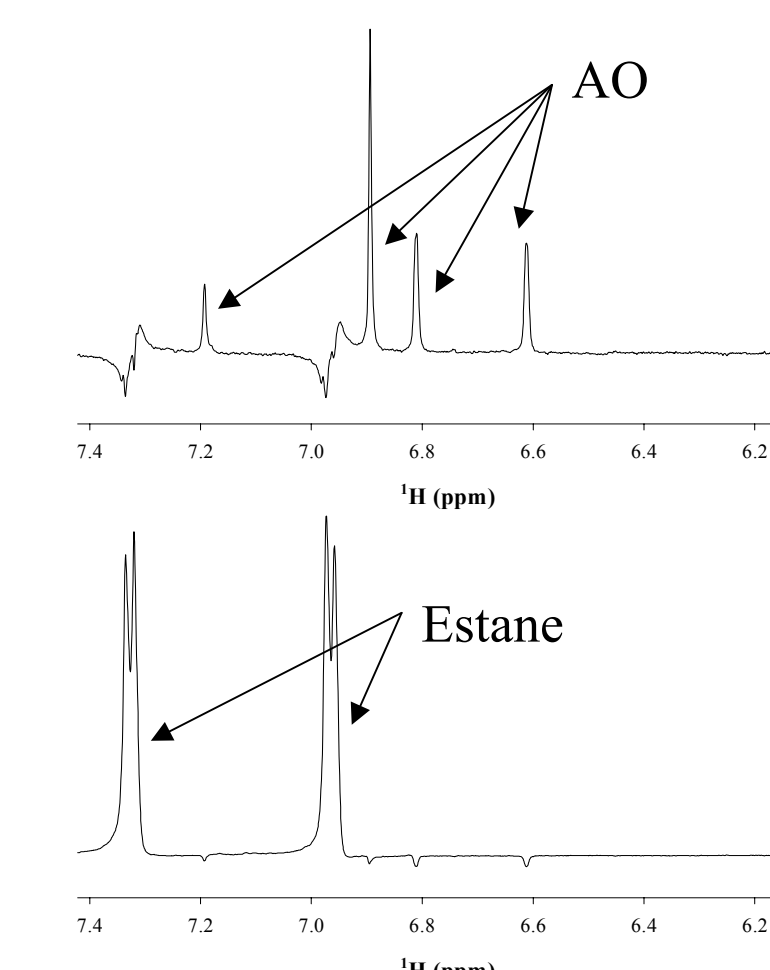
• DECRA can resolve antioxidants (AO), unreacted precursors, unaged polymer material and degraded polymer material within polymer mixtures.

• Some pure component spectral “mixing” observed.

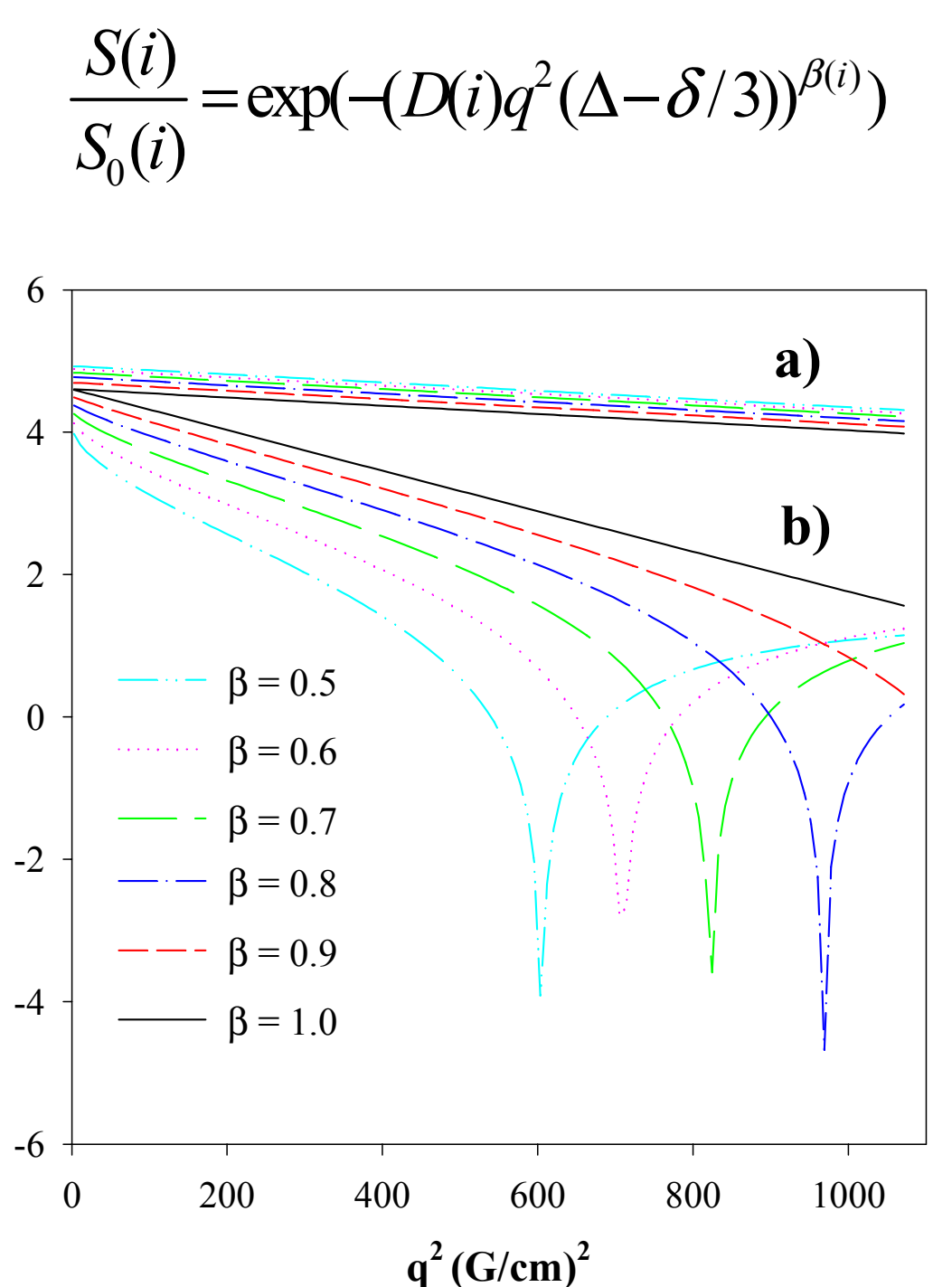
• Is this “mixing” an effect of multi-component relaxation? What are the impacts of polydispersity on the DECRA analysis. Proportionality assumption not fulfilled.

• Simulations of PFG data sets with summations of decay constants were created to address these issues.

Estane Film: Vanox/Irganox AO



Kohlrausch-Williams-Watts (KWW) distribution



## DECRA Theory

For 2 proportional data sets an **unambiguous** solution can be obtained!

$$\mathbf{A} = \mathbf{C}\mathbf{P}$$

$$\mathbf{B} = \mathbf{C}\alpha\mathbf{P}$$

α = diagonal scaling matrix

$$\mathbf{A}(\mathbf{P})^+ \alpha = \mathbf{B}(\mathbf{P})^+$$

$$\mathbf{A}\mathbf{Z}\alpha = \mathbf{B}\mathbf{Z}$$

where

$$\mathbf{Z} = (\mathbf{P})^+$$

$$\mathbf{A}\mathbf{Z}\alpha = \mathbf{B}\mathbf{Z}$$

$$\mathbf{A} = \overline{\mathbf{U}}\mathbf{S}\mathbf{V}^T$$

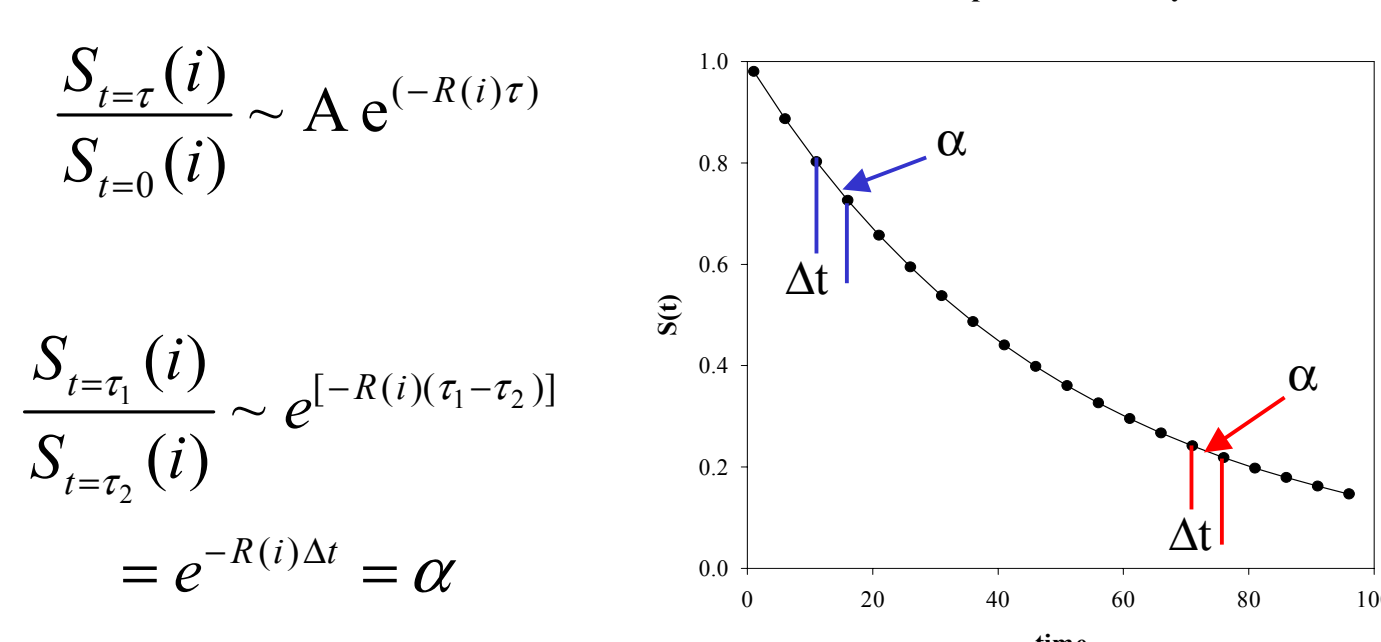
In order to solve this both **A** and **B** must be square!  
Use a common space to project both data files, using SVD.

Standard eigenvector problem!

$$\mathbf{Z}^* \alpha = (\overline{\mathbf{U}}^T \mathbf{B} \overline{\mathbf{V}} \mathbf{S}^{-1}) \mathbf{Z}^*,$$

$$\mathbf{Z}^* = \overline{\mathbf{S}} \mathbf{V}^T \mathbf{Z}$$

For equally spaced data along exponential decay, the proportionality constant α is the same for any pair of related data. In this case the data matrices **A** and **B** can be formed from a single data set!



## Estane/Antioxidant Studies

